

Studies on Epoxidized Rubber Seed Oil as Plasticizer for Acrylonitrile Butadiene Rubber

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ABSTRACT: The application of rubber seed oil (RSO) and epoxidized RSO (ERSO) as a plasticizer in acrylonitrile butadiene rubber (NBR) was studied using RSO and ERSO with different levels of epoxidation. The results indicated that ERSO could be used as a less leachable and low volatility plasticizer for NBR. The use of ERSO in NBR gave better abrasion resistance whereas the tensile strength and tear

strength were comparable to those vulcanizates that contained dioctyl phthalate as a plasticizer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 668–673, 2003

Key words: epoxidation; nitrile rubber; plasticizer; rubber seed oil

INTRODUCTION

The rubber tree (*Hevea brasiliensis*) is widely used as a source of natural rubber, and its seed has been found to be rich in oil. Among the ancillary resources obtained from rubber plantations (wood, seeds, and honey), seed has the greatest potential use.^{1–3} Although there is a variation in the oil content of the seed from different clones, the average oil yield is about 42% of the weight of the dried kernel. The fatty acid composition is fairly constant, irrespective of the oil source.⁴ The composition and characteristics of rubber seed vary with the planting location and clone.⁵ Fresh seed contains about 65% kernel and 35% shell.⁶ Rubber seed oil (RSO) is a light yellow colored, semidrying type of oil, the properties of which are given in Table I. The oil contains about 18–22% saturated and 78–82% unsaturated higher fatty acids. The composition of the fatty acids present in RSO is given in Table II.

There are various industrial applications for RSO. The oil is used to produce factice.⁷ Vijayagopalan and Gopalakrishnan⁸ reported the epoxidation of RSO with hydrogen peroxide and acetic acid. Epoxidized RSO (ERSO) is used in formulations for anticorrosive coatings, adhesives, and alkyd resin coatings.⁹ Studies on the practical utilization of RSO revealed that it has strong potential to be a substitute for linseed oil in alkyd production.⁹ It is also suitable for the production of low quality soap.¹⁰ The properties of RSO resemble those of linseed oil. RSO was therefore conceived as having strong potential for wholly or partially replacing linseed oil in alkyd production.¹¹ The

use of ERSO and its lead and barium salts as heat stabilizers for poly(vinyl chloride) has been reported by researchers from Nigeria.^{12–14} Aigbodin et al.¹⁵ have reported the use of RSO and ERSO in natural rubber compounds for improving the processability characteristics and physicomechanical properties.

Because nitrile rubber is polar in nature, mostly ester-type plasticizers such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) are used for its compounds. In applications such as oil seals and O-rings, nitrile rubber vulcanizates lose most of their plasticizers through leaching and volatilization, causing failure of the product. ERSO, being polar in nature and having higher molecular weight than DOP/DBP, is expected to be compatible with nitrile rubber and function as a good plasticizer for it. In this article we report the results of the evaluation of ERSO in nitrile rubber compounds in comparison with DOP.

EXPERIMENTAL

Acrylonitrile butadiene rubber (NBR) with 33% acrylonitrile content was purchased from local sources. RSO, which was prepared by an expulsion process of

TABLE I
Properties of Rubber Seed Oil

Parameters	Range of Values
Acid value	4–40
Saponification value	190–195
Iodine value	132–141
Hydroxyl value	12–32
Unsaponifiables (%)	0.5–1
Refractive index at 40°C	1.466–1.469
Specific gravity	0.92–0.93
Titer (°C)	28–32

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TABLE II
Composition of Fatty Acids in Rubber Seed Oil

Fatty Acid	Content
	(%)
Palmitic acid	11
Stearic acid	12
Arachidic acid	1
Oleic acid	17
Linoleic acid	35
Linoleinic acid	24

dried kernels, was obtained from Virudhunagar. ERSO with a different epoxidation level was prepared from RSO using hydrogen peroxide and acetic acid as epoxidizing agents at 58–60°C.⁸ The epoxidation level was determined by the acidimetric method.¹⁶ All other chemicals used in this study were of rubber chemical grade. The formulations of the prepared compounds are given in Table III. RSO, ERSO with different levels of epoxidation, and DOP were used as plasticizers in these compounds at 7 parts per hundred rubber (phr) loading for a total filler content of 80 phr carbon black. This formulation is a typical one for O-rings and oil seals with a 65–68 Shore A hardness range.

The compounds were prepared using a 150 × 300 mm laboratory two-roll mixing mill at a friction ratio of 1:1.25. The optimum cure time (t_{90}) at 150°C was determined using a Monsanto R-100 rheometer. The Mooney scorch time (t_5) at 120°C was determined using a Mooney viscometer (SMV-202, Shimadzu). The compounds were vulcanized with the optimum cure time at 150°C in an electrically heated hydraulic press. Dumb-bell shaped test pieces were punched out

from the vulcanized sheet along the direction of the grain and tested for tensile properties according to ASTM D 412-80 using a Zwick 1474 model Universal testing machine. Tests such as the hardness (ASTM D 2240-97), abrasion loss (DIN 53516-77), compression set (ASTM D 395-98), and resilience (ASTM D 1054-91) were also performed. The aging resistance of the vulcanizate was determined by testing the tensile properties of the samples before and after aging at 70°C for 7 days in a hot air circulating oven.

The oil resistance and leachability of the sample were studied by keeping the sample in ASTM No. 3 oil for 168 h at room temperature.¹⁷ A rectangular specimen (25 × 50 × 2 mm) was used for this study. The initial mass of the sample was measured, and then it was immersed in 100 mL of ASTM No. 3 oil at room temperature for 168 h. After this period, the specimen was removed, dipped in acetone, blotted lightly with filter paper, and placed immediately in a tared, stoppered weighing bottle in which the mass of each of the swollen samples was determined. The extent of swelling, as indicated by the mass of the ASTM No. 3 oil absorbed by the sample, was calculated using the following equation:

$$\text{oil absorption (\%)} = \frac{(M_2 - M_1)}{M_1} \times 100$$

where M_1 is the initial mass of the specimen and M_2 is the mass of the specimen after swelling in oil.

To assess the leaching loss, the oil-swollen samples were dried at 70°C for 48 h, cooled in a desiccator, and weighed (M_3). The leaching loss was calculated as

TABLE III
Formulation of Compounds

Ingredients	Formulations						
	N1	N2	N3	N4	N5	N6	N7
Nitrile rubber	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1	1	1	1	1	1	1
TMTD	2	2	2	2	2	2	2
Sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TDQ	1.5	1.5	1.5	1.5	1.5	1.5	1.5
IPPD	1	1	1	1	1	1	1
MT-black	50	50	50	50	50	50	50
SRF black	30	30	30	30	30	30	30
DOP	7	—	—	—	—	—	—
RSO	—	7	—	—	—	—	—
ERSO 1 (0.4%)	—	—	7	—	—	—	—
ERSO 2 (0.9%)	—	—	—	7	—	—	—
ERSO 3 (1.75%)	—	—	—	—	7	—	—
ERSO 4 (2.7%)	—	—	—	—	—	7	—
ERSO 5 (5.2%)	—	—	—	—	—	—	7

MBTS, Mercaptodibenzothiazyl disulfide; TMTD, tetramethyl thiuram disulfide; TDQ, 2,2,4-trimethyl 1,2, dihydroquinoline; IPPD, isopropyl paraphenylene diamine; MT black, medium thermal black; SRF black, semireinforcing furnace black; DOP, dioctyl phthalate.

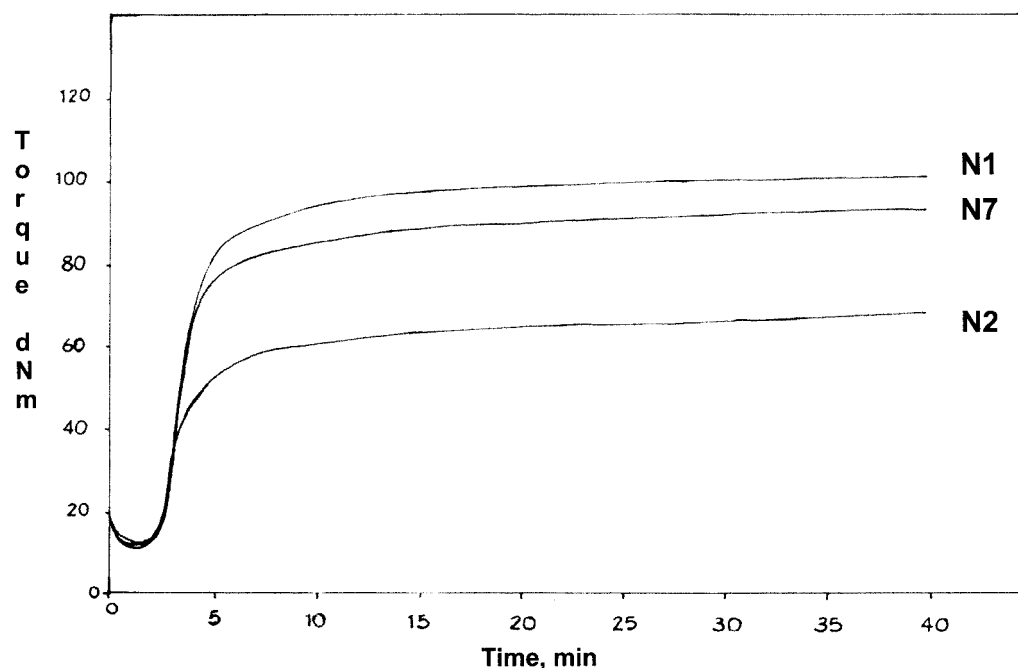


Figure 1 Rheographs of compounds N1, N2, and N7.

$$\text{leaching loss (\%)} = \frac{(M_1 - M_3)}{M_1} \times 100$$

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

The extent of crosslinking of the vulcanizates was determined through swelling studies by keeping the sample in chloroform for 48 h at 25°C per the method reported by Ellis and Welding.¹⁸

Samples of approximate 10-mm diameter and 2.5-mm thickness and weighing approximately 0.3 g were punched from the central portion of the vulcanized film and allowed to swell in chloroform at 25°C. Then the swollen samples were taken out after the equilibrium swelling period, blotted with filter paper, and quickly weighed in a stoppered weighing bottle. The samples were dried in an oven for 24 h at 70°C and then in a vacuum, and they were weighed after allowing them to cool in a desiccator. Duplicate readings were taken for each sample. The volume fraction of rubber (V_r) in the swollen sample was calculated by the method reported by Ellis and Welding,¹⁸ which takes into account the correction of the swelling increment with the duration of immersion after the equilibrium is attained:

where T is the weight of the test specimen; D is its deswollen weight; F is the weight fraction of the insoluble component; A_0 is the weight of the absorbed solvent, corrected for the swelling increment; ρ_r and ρ_s are the densities of the rubber and solvent, respectively; ρ_r (NBR) = 0.95 g cm⁻³; and ρ_s (chloroform) = 1.48 g cm⁻³.

The V_r value can be taken as a measure of the crosslink density. The volatilization loss of plasticizer was determined by heating the weighed sample in an air circulating oven at 100°C for 7 days and by thermogravimetric analysis.

$$\text{volatilization loss (\%)} = \frac{(M_1 - M_4)}{M_1} \times 100$$

where M_4 is the final weight.

TABLE IV
Cure Characteristics

Properties	N1	N2	N3	N4	N5	N6	N7
Optimum cure time (min) at 150°C	6.5	9.5	7.0	9.0	7.5	8.0	8.0
Scorch time (min) from rheograph	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Mooney scorch time (min) at 120°C	15.5	15.0	14.8	13.8	13.5	14.4	13.8
Minimum rheometric torque (dNm)	10	10	11	10	12	10.5	10.5

TABLE V
Physical and Mechanical Properties of Vulcanizates

Properties	N1	N2	N3	N4	N5	N6	N7
Tensile strength (MPa)	10.65	10.3	10.86	10.86	10.95	10.55	10.45
Elongation at break (%)	425	491	454	406	447	449	426
Modulus (MPa)							
100%	3.64	2.95	3.46	4.21	3.84	3.29	3.29
300%	9.24	8.05	9.15	9.62	9.7	8.9	9.0
Tear strength (kNm ⁻¹)	47.2	49.8	49.2	46.4	47.8	48.4	46.8
Compression set (%)	8.17	10.52	10.28	10.14	10.40	8.08	8.37
Din abrasion loss (mm ³)	102	93	98	97	95	94	98
Heat buildup (°C)	45	51	49	47	47	45	43
Hardness (Shore A)	68	66	66	67	67	66	66
Rebound resilience (%)	45.7	42.8	43.4	44	44.2	45.9	46.5

RESULTS AND DISCUSSION

Cure characteristics

Figure 1 shows the rheographs of the compound containing DOP, RSO, and ERSO (5.2%). It is evident from the figure that compounds N7 and N2 both have a lower maximum rheometric torque value compared to compound N1, indicating better plasticizing action of these materials. Compound N2 showed the lowest maximum rheometric torque value, probably because of the combined effect of higher plasticizing action and a lower extent of crosslinking. The cure characteristics of the compounds given in Table IV indicate that the compound containing RSO (N2) and those containing ERSO (N3–N7) have higher cure times than the control compound containing DOP (N1). Different levels of epoxidation of the RSO did not show proportional changes in the cure time. All seven compounds had the same scorch time (t_{s2}) from the rheograph. The Mooney scorch value (t_5) at 120°C is also comparable for the seven compounds. The increase in the cure time of the compounds containing RSO and ERSO may be due to partial utilization of sulfur for reacting with the unsaturated fatty acids present in these materials.

Physical and mechanical properties

From Table V it is seen that the vulcanizates containing ERSO showed comparable tensile strengths and

moduli with that containing DOP. The tear strength values were marginally higher for compounds N2 and N3, which may be due to the higher elongation at break of these vulcanizates. Compounds N2–N5 have a lower extent of epoxidation (<2%) and these compounds generally showed a higher compression set and heat buildup and lower hardness and rebound resilience compared to the control compound N1, which contained DOP as the plasticizer. Among these, compound N2 containing RSO showed lower tensile strength, modulus, and rebound resilience and higher elongation at break and compression set. A possible explanation for this observation is that RSO contains about 78–82% unsaturated fatty acids (Table II), which can compete with the polymer for reacting with sulfur. Because the dosage of sulfur in the formulation is low, there is a chance that the presence of unsaturated fatty acids affects the extent of crosslinking of the rubber phase. This argument is further supported by the fact that at higher levels of epoxidation of the RSO (e.g., compounds N6 and N7) some of the properties that are more dependent on the extent of crosslinking showed some improvement. The V_r values given in Table VI further support this view. At higher levels of epoxidation, properties such as the compression set and heat buildup were lower and the rebound resilience higher compared with those of the other compounds. The physical and mechanical properties of compounds N2–N5 did not show a regular change with the epoxy content of the oil. This is expected to be

TABLE VI
Swelling, Leaching, and Volatilization Behavior of Vulcanizates

Parameter	N1	N2	N3	N4	N5	N6	N7
Mass of ASTM no. 3 oil absorbed (%)	1.73	2.00	1.90	1.82	1.82	1.83	1.78
Leaching loss (%)	0.62	0.29	0.27	0.29	0.19	0.18	0.18
Volatilization loss (%)	1.71	1.58	1.58	1.58	1.55	1.48	1.40
V_r value	0.186	0.167	0.180	0.180	0.183	0.185	0.185

V_r = volume fraction of rubber.

TABLE VII
Tensile Properties after Aging at 70°C for 168 h

Properties	N1	N2	N3	N4	N5	N6	N7
Tensile strength (MPa)	11.1	10.78	11.38	11.0	12.07	11.30	11.55
Retention (%)	104.2	104.7	104.8	101.3	110.2	107.1	110.5
Elongation at break (%)	323	431	347	330	375	393	377
Retention (%)	76	87.8	76.4	81.3	83.9	87.5	88.5
100% Modulus (MPa)	4.88	3.47	4.5	4.9	4.62	3.47	4.21
Retention (%)	134.1	117.6	130.1	116.4	120.3	105.5	127.9
300% Modulus (MPa)	10.3	9.35	10.8	10.03	11.23	9.3	10.6
Retention (%)	111.5	116.1	118.0	104.3	115.8	104.5	117.8

due to the fact that the level of epoxidation of the oil used in these compounds is rather low. However, use of ERSO in place of DOP is not going to adversely affect the properties that are more relevant to applications such as oil seals and O-rings.

The Din abrasion resistance of compounds N2–N7 was better than control compound N1. It was shown that the use of a higher dosage of stearic acid (6 phr) in tread formulations enhanced the abrasion resistance.¹⁹ The higher fatty acid soap formed during vulcanization was believed to act as a better lubricant, facilitating slippage of the molecular chains past each other under an applied load in such cases. In the present case also, a similar mechanism is expected to operate in compounds containing RSO and ERSO, resulting in better abrasion resistance.

Aging resistance

Use of vegetable oils such as linseed oil is reported to enhance the aging/ozone resistance in polychloroprene-based vulcanizates.^{20,21} A similar observation in nitrile rubber was reported by Nandan et al.²² Even though the exact mechanism of the action of these oils for such an observation is not fully understood, it is possible that the oil acts as a carrier for the antidegradants in the compound, helping them to be brought to the surface where the oxidation mostly occurs. From Table VII it can be seen that the aging resistance of the compounds containing RSO and ERSO is comparatively better than that containing DOP, as indicated by both better mechanical properties (tensile strength, elongation at break, and 300% modulus) and higher retention of these properties of the vulcanizates after aging at 70°C for 7 days.

Swelling and leaching behavior

A change in the dimension of vulcanized rubber when it comes in contact with oil is a matter of high concern in designing compounds for products such as oil seals. Vulcanized rubber swells in oil by absorbing it. At the same time, certain ingredients such as plasticizers and antidegradants get leached out of the vulcanizates

during the swelling process. The data given in Table VI indicate that vulcanizates N2–N7 swell more in ASTM No. 3 oil than control sample N1 by absorbing the oil. However, as the level of epoxidation of the RSO increases, the extent of swelling decreases. The higher level of swelling of samples N2–N7 compared to control sample N1 is due to the lower extent of crosslinking of their vulcanizates, as is evident from the lower V_r values of these samples given in Table VI. The leaching loss, as indicated by the weight loss of the samples swollen in ASTM No. 3 oil, was considerably lower for vulcanizates N2–N7 compared to sample N1, which contained DOP as the plasticizer. The lower leaching loss of samples N2–N7 is expected to be attributable to the higher molecular weights of RSO and ERSO, which are approximately 877 and 960, respectively, compared with that of DOP, which is 390.²³

Volatilization loss and thermal stability

The use of softeners with very low molecular weight is limited by their high volatility. During vulcanization or service of the product, loss of softener takes place.²⁴

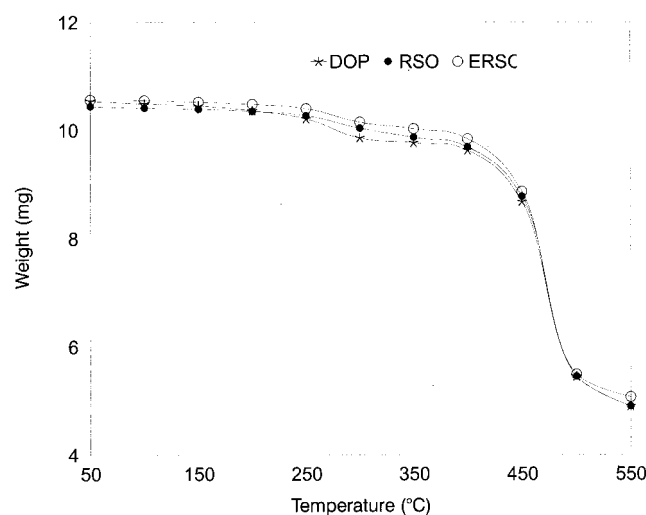


Figure 2 A thermogram of NBR vulcanizates containing DOP, RSO, and ERSO as plasticizers.

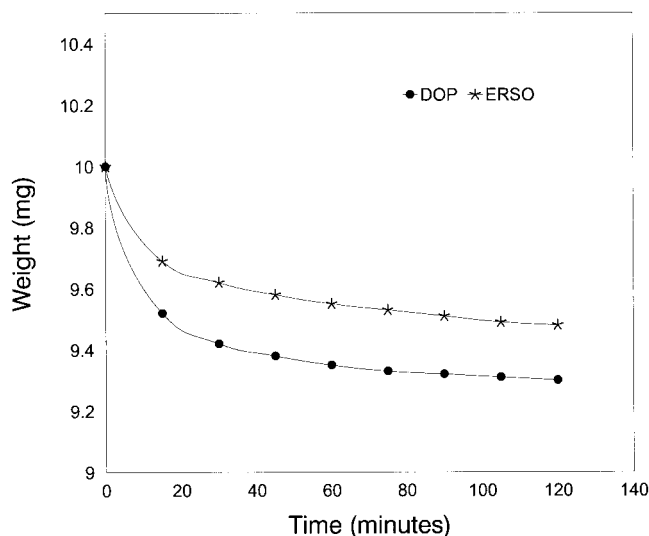


Figure 3 A thermogram at 250°C of NBR vulcanizates containing DOP and ERSO as plasticizers.

During heating at a higher temperature, the lower molecular weight plasticizer is volatilized and escapes from the vulcanizate, leading to shrinkage and failure of the products such as O-rings. The volatilization loss of vulcanizates N2–N7, when heated at 100°C for 168 h, is much lower than that from control sample N1 (Table VI). This is further evident from the thermogram given in Figure 2. The weight of the sample retained up to 450°C in a heating cycle of 5°C/min is more for the vulcanizate containing 2.7% ERSO than that containing RSO or DOP. The thermograms at isothermal conditions (Fig. 3) also show lower heating loss for the sample containing 2.7% ERSO at 250°C. These observations indicate that RSO and ERSO impart better thermal stability to NBR vulcanizates compared to DOP.

CONCLUSIONS

The results of the present study indicated that RSO and ERSO could be used as less leachable and low volatile plasticizers for nitrile rubber. Use of ERSO in nitrile rubber gave better abrasion resistance whereas the tensile strength and tear strength were comparable

to those vulcanizates that contained DOP as a plasticizer.

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